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(54) Title: POLYALPHAOLEFIN PLASTISIZERS FOR ELASTOMERS

(57) Abstract: The present invention relates to polyalphaolefin plastisizers for elastomers, and elastomer compositions containing polyalphaolefins. Polyalphaolefins may be used as plastisizing agents in elastomers and blends containing elastomers to plastisize the hardness of the product and to provide more flexible products with a lower residual compression suitable for lower working temperatures. Elastomer composition of the invention containing a plastisizing agent comprises between 20 and 95 % by weight of an elastomer or a mixture of elastomers, and between 5 and 60 % by weight of polyalphaolefin or a mixture of polyalphaolefins.

Polyalphaolefin plastisizers for elastomers

5 The present invention relates to polyalphaolefin plastisizers for elastomers, and elastomer compositions containing polyalphaolefins. Polyalphaolefins may be used as plastisizing agents in elastomers and blends containing elastomers to plastisize the hardness of the product and to provide more flexible products with a lower residual compression suitable for lower working temperatures.

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Plastisizers are commonly used in elastomers to lower the raw material costs of the products and to improve the processibility thereof. Addition of a plastisizer is used to improve the collapse resistance of an article made of rubber or thermoplastic elastomer exposed to oil in the environment. Plastisizers present in the product reduce the ability thereof to absorb additional hydrocarbons. Most common plastisizers are compounds based on mineral oil.

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Patent application FI 971338 discloses coatings of structures and profiled articles containing a mixture of thermoplastic elastomer with a non-elastomeric polyolefin, in general with homopolymers or random copolymers of propylen. An oligomer of poly- α -olefine type is used as polyolefin plastisizer in a matrix plastic (EPR, EBR, EPBR, PBR, SBR, EPM, EPDM). The monomers used comprise at least 3 carbon atoms, preferably 6 to 12 carbon atoms.

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Patent publication EP 300 689 discusses mixtures containing oligomeric polyalphaolefin, and an olefin elastomer.

The object of the present invention is to provide polyalphaolefin plastisizers for elastomers, and elastomer compositions containing polyalphaolefins.

The characteristic features of the polyalphaolefin plastisizers for elastomers, and elastomer compositions containing polyalphaolefins of the invention are disclosed in the appended claims.

- 5 It has been found that colourless, odourless, tasteless and clear polyalphaolefins may be used as plastisizing agents in elastomers. Suitable polyalphaolefins include polyalphaolefin oils. In this connection, polyalphaolefin oil means an oil, preferably a food grade hydrogenated oil consisting of the polymerization product of a polyalphaolefin or a mixture of polyalphaolefins, having a molecular weight between 400 and 1000
10 g/mol. Suitable alphaolefins include butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene, preferably decene. A particularly preferable polyalphaolefin is food grade polydecene.

- 15 The content of polyalphaolefin oil or oils in the composition of the invention varies between 5 and 60 %.

Suitable elastomers include the following rubber mixtures (a), thermoplastic elastomers (b) and vulcanizates thereof (c), and silicones (d):

- 20 (a) Normally plastisized rubbers (elastomers) used in health care applications and in automobile industry, and for cables:
EPR = ethylene-propylene rubber
EPDM = ethylene-propylene-diene rubber
NR = natural rubber
25 IIR = butyl rubber
ACM/EAM = polyacrylate rubber
SBR = styrene-butadiene rubber
1,2-sPB = 1,2-syndiotactic polybutadiene rubber.

(b) Plastisized thermoplastic elastomers; polypropylene commonly as a crystalline thermoplastic in a mixture.

SBC = styrene-butadiene blockcopolymers,

unhydrogenated version	hydrogenated version
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SBS	SEBS
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SB	SEB
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SI	SEP
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EPR, EPDM, NR, IIR, 1,2-sPE = as above.

(c) Thermoplastic vulcanizates:

Vulcanization is accomplished while mixing either with a sulfur compound, organic peroxide or with a phenolic resin depending on the type of the elastomer.

(d) Silicones.

No plastisizers may be used in crystalline plastics since the crystalline structure will not tolerate the presence of an oil. Unplastisized plastics typically include polycarbonates, polyolefins (PE and PP), polyamides and polyuretanes. Compounding these plastics with elastomers provides in certain cases mixtures that may be plastisized.

In the compositions of the invention, the elastomers may be unvulcanized or partly or totally vulcanized. Particularly preferable elastomers are the following polymers and mixtures thereof:

- ethylene-propylene-diene rubber
- ethylene-propylene rubber
- styrene-butadiene rubber
- 1,2-syndiotactic polybutadiene rubber

- natural rubber
- polybutyl rubber
- styrene-isoprene-styrene blockcopolymer
- styrene-butadiene-(styrene) blockcopolymer
- 5 - styrene-ethylene-butene-styrene blockcopolymer.

The composition of the invention contains from 20 to 95 % by weight of elastomer or mixture of elastomers. The ratio of polyalphaolefin oil to the elastomer is 0.05 to 1.5.

10 In addition to the elastomers, the compositions may comprise thermoplastics, inorganic fillers, other plastisizers based on mineral oil, antioxidants, pigments, agents protecting against ultraviolet light, agents deactivating metals, flame retardants, conductive fillers, and vulcanizing chemicals.

15 With respect to performance, polyalphaolefins have several advantages in plastisizing applications. For instance:

- Superior heat resistance is an important feature in medical apparatus and device applications requiring repeated sterilization or heating of the article in a micro-wave oven, for instance as a component of a food tray. There are also other appli-
20 cations profiting from the high heat resistance, such as cable applications and engine room applications in automobile industry.

- Strictly limited composition, that is, a narrow molecular weight distribution al-
25 lows for the selection of the desired molecular weight, thus minimizing the evaporation effects of the plastisizing agent or oil. In addition, the flash point of polyalphaolefin is generally higher at the desired viscosity than that of conventional mineral oils, this being favourable for processing. With respect to its qual-

ity, polyalphaolefin is a pure product, thus facilitating the approval by the authorities.

- A low working temperature is an important characteristic of polyalphaolefins. They crystallize at very low temperatures, thus making possible to lower the brittle temperature of rubber or a thermoplastic elastomer. This is advantageous particularly for styrene elastomers. In applications of the automobile industry, the required lowest working temperature is commonly below -40°C .

In addition, polyalphaolefins have the following advantages in comparison with a mineral oil based plastisizer:

a) Chemical properties

A typical feature of polyalphaolefins is the chemical purity thereof, that is the lack of aromatic, naphthalenic, paraffinic (with the exception of isoparaffinic) components commonly present in mineral oils. Moreover, mineral oil typically contains sulfur and other heteroatoms absent from synthetic polyalphaolefins.

Elastomers plastisized with polyalphaolefin oil are more heat stable since heteroatoms causing autocatalytic decomposition are absent. The use of relatively expensive antioxidants may be reduced to provide the required thermal ageing properties. In addition, the original colour of elastomers plastisized with polyalphaolefins is purer than that of products plastisized with mineral oils, thus allowing for the production of lighter products by means of pigments without using paints to provide a pure white colour. Compared to painting, pigments are a preferable alternative. Moreover, colour fastness in pigmented elastomers is clearly better when a polyalphaolefin plastisizer is used instead of mineral oil. For transparent elastomer products, an advantage is the

better preservation of transparency for instance of the tubing of health care apparatuses being sterilized.

5 Polyalphaolefins are particularly advantageous as plasticizers for elastomeric insulating materials of cables and conductors. Polar impurities present in mineral oil lower the loss factor causing increasing power losses in power transmission for medium and high voltage insulating materials. With respect to electrical properties, polyalphaolefin is comparable to commonly used insulating materials, polyethylene and EP(D)M rubber.

10

Aromatic components present in mineral oil dissolve styrene blocks present in polystyrene containing elastomers, thus lowering the tensile strength. Polyalphaolefin has no influence on polystyrene blocks since it is free of aromatic components.

15

b) Physical properties

The molecular weight distribution of polyalphaolefins is very narrow compared to that of mineral oils that are originally distillates. This narrow molecular weight distribution brings about several advantages. Of these, the most important for elastomers is the low weight loss at increased temperatures. A polyalphaolefin oil and mineral oil having identical viscosities differ considerably from each other with respect to weight loss in favour of polyalphaolefin. Volatile oils cause following problems in practical applications of elastomers:

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- volatile oils cause fogging of the glass surfaces and bad odour in the interior of an automobile,
- elastomers in the engine room of an automobile become hard and brittle,
- elastomers become hard when sterilized in an autoclave.

These problems may be considerably reduced by using polyalphaolefin oils as plasticizers.

5 Further, the advantages of polyalphaolefin oils include the lack of odour and the lower flash point at a constant viscosity, thus contributing to process safety.

Compared to naphthenes and aromates, isoparaffins and paraffins have lower dissolving powers in elastomers, which directly influences the compatibility of the oils with elastomers. The absence of relatively heavy molecules from polyalphaolefin oils
10 makes a polyalphaolefin oil more preferable than mineral oils, the final result with respect to compatibility being equally good.

As is known, polyalphaolefins have a very low solidification point, about -60 °C, whereas the solidification point of paraffin oils is about -15 °C, that of naphthalene oil
15 being about -30 °C.

The properties of polyalphaolefin plasticizers are best preserved at extremely low temperatures. This is important for instance for buffering rubber strips of automobiles and protective rubbers of joints.

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Polyalphaolefins have a very high viscosity index compared to mineral oils. This is important in processing of elastomers. Particularly when elastomers are mixed at high temperatures, the viscosity of the mixture will not decrease as much as that of mixtures containing mineral oils, and thus higher shear forces are provided for mixing,
25 thus improving the dispersion of components. This has a direct effect on almost all performance values of elastomers. Depending on the composition, the following factors are improved:

- tensile strength
- elongation

- effectivity of flame retardants
- amount of the filler may be increased.

5 In practice, the compositions of the invention containing polyalphaolefins may be used as interior elastomers of automobiles such as seals in passages to the engine room, rubbers in the engine room such as tubes and seals, buffering rubber strips, protective rubbers of joints, in medical apparatuses and devices such as the tubings and seals of medical instruments, seals of food packages, isolating materials of cables, cable jackets, and further, in elastomeric articles that are generally white, and in
10 applications being demanding with respect to transparency.

Elastomers and plastics used in medical applications and having a very high compatibility with polyalphaolefins include:

15	Type of plastic	Most common plastisizers	Compatibility with polyalphaolefins
	PP/EPDM	Paraffin oil, naphtalene oil	Very high
	PP/SBC	Paraffin oil, naphtalene oil	Very high

20

Next, the use of polyalphaolefins as plastisizing agents in plastics is discussed in more detail.

1. Use of polyalphaolefins in elastomers:

25 PP/EPDM or PP/EPR blend

Raw material	% , by weight	
EPDM or EPR	5 to 80	
Polypropylene	15 to 90	
5	Plastisizer 1	5 to 30 polyalphaolefin
	Plastisizer 2	0 to 35 mineral oil
	Antioxidant	0 to 0.3
	Peroxide	0 to 0.1 di-tert-butyl peroxide
	Internal lubricant	0 to 0.2 magnesium stearate
10		

2. Use of polyalphaolefins in styrene based thermoplastic elastomer: SEBS blend.

The combination PP/SEBS is generally used in those applications of styrene elastomers that are demanding with respect to working temperature and environmental pollution.

Raw material	% by weight	
SEBS	30 to 50	
20	CaCO ₃	0 to 20
	Polypropylene	0 to 30
	Plastisizer 1	5 to 30 polyalphaolefin
	Plastisizer 2	0 to 35 mineral oil
	Antioxidant	0 to 0.3
25		

Typical medical uses of elastomers are syringes and needles, intravenous urinary catheters, dosage tubings and devices, clinical cardiac valves and vessel implants, disposable packages and trays.

The composition of the invention has several advantages. The glass transition temperature of the elastomer and plastic is lowered, thus making the products very suitable to applications requiring good low temperature resistance properties (cables, exterior parts of automobiles). Further, the evaporated amounts of organic compounds are lowered, being advantageous for medical applications and for interior elastomers of automobiles. The products are colourless and transparent. The products resist sterilization and exposure to high temperatures for extended periods of time without losing their properties.

10

Polyalphaolefin may be mixed with elastomers and plastics during the production thereof. In this manner, elastomer and plastic products particularly suitable for medical and medicinal apparatus applications are obtained. Medical applications have high special requirements on materials, such as resistance to sterilization. These requirements are restricted in no way by the composition of the invention.

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The invention will now be illustrated in more detail with the following examples without wishing to limit it to these exemplary solutions.

Example 1

**Elastomer for medical, automobile industry, and cable applications:
PP/EPDM or PP/EPR blend**

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Raw material	% by weight	Products
EPDM or EPR	59.8 / 59.5	Vistalon 805 / Nordel IP 3745P
Polypropylene	29	Escorene PP 4152
10 Plastisizer 1	10	polydecene
Plastisizer 2	0	mineral oil
Antioxidant	0.3	Irganox B-225
Peroxide	0.1	di-tert-butyl peroxide
Internal lubricant	0.2	magnesium stearate

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With the composition of the example, good processing characteristics and a Shore A hardness of 85 are attained. Thermal ageing properties of the mixture are also especially good.

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Example 2

Styrene based thermoplastic elastomer: SEBS blend

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The example is directed to a basic SEBS blend. The combination PP/SEBS is generally used in those applications of styrene elastomers that are demanding with respect to working temperature and environmental pollution.

Raw material	% by weight	Products:
SEBS	30	Shell Kraton G-1651
CaCO ₃	15	Omycarb 2A, OMYA
Polypropylene	13.4	Escorene PP 4152
5 Plastisizer 1	35	polydecene
Plastisizer 2	0	mineral oil
Antioxidant	0.3	Irganox B-225

10 The ability to plastisize SEBS elastomers greatly depends on the styrene content thereof. An elastomer with a low styrene content accepts a plastisizer in an amount that is more than 1.5 times its own weight.

Example 3

15 Glass transition temperature

The effect of polyalphaolefin plastisizers on low temperature resistance was studied by means of the glass transition temperature T_g . As a reference sample, a common plastisizer, i.e. paraffin oil was used. The samples to be studied were the formulations
20 of Examples 1 and 2.

Table I Glass transition temperature of elastomers

Polyalphaolefin oil, % by weight	SEBS/PP	EPDM/PP
10	-46	-33
20	-51	-39
30	-56	-41
40	-58	-45
Paraffin oil, 40 % by weight	-52	-42

The results show that glass transition temperatures are lowered more by polyalphaolefin oil than by paraffin oil. For SEBS formulation, the glass transition temperature was lowered considerably more, that is, by -6°C , whereas for EPDM formulation, it was -3°C lower. Due to these superior low temperature resistance properties, thermoplastic elastomers plastisized with polyalphaolefin oil are very suitable for the production of cables and automobile components.

Example 4

10 Colour and colour stability

Original colours of the mixtures were considerably better with polyalphaolefin oil than with paraffin oil. Especially the colour of EPDM mixtures was clearly improved by using polyalphaolefin oil. For both tested elastomers (EPDM and SEBS), the colour change was by dE 2.5 better compared to paraffin oil before ageing. Paraffin oil made the colour of the samples yellowish. During ageing, the colour change was identical in all samples independent of the plastisizer used.

Table II Colour change dE (125°C)

	SEBS		EPDM	
	100 h	200 h	100 h	200 h
Polyalphaolefin oil	1.8	1.8	4	4
Paraffin oil	0.9	0.6	3.8	4

20

The use of a polyalphaolefin oil as the plastisizer is particularly preferable for the production of clear white elastomer products. The translucency of translucent elastomers suitable for instance for health care applications is better preserved by using a polyalphaolefin oil instead of mineral oil.

Example 5**Loss on evaporation**

- 5 By comparing several plastisizers, it was found that by using a polyalphaolefin oil the volatile matter (100 h, 125 °C) was 40 to 50 % lower than that obtained with paraffin oil. The difference increases with time. Due to this lower volatile matter, products containing a polyalphaolefin as plastisizer are very suitable for the production of materials for e.g. the interior of an automobile.

10

Table III Volatile matter [% by weight] at 125 °C

	Polyalphaolefin oil	Paraffin oil
100 h	0.59	1.19
240 h	0.86	2.25

Example 615 **Sterilizability**

Thermoplastic elastomers were sterilized in an autoclave for 15 minutes at 121 °C. Elastomers may be hardened by autoclaving as the plastisizing oils are evaporated. This was not the case for polyalphaolefin oils due to the low volatile matter thereof.

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Claims

1. Elastomer composition containing a plastisizing agent, **characterized** in that the composition comprises between 20 and 95 % by weight of an elastomer or a mixture of elastomers, and between 5 and 60 % by weight of polyalphaolefin or a mixture of polyalphaolefins.
2. Composition of Claim 1, **characterized** in that the polyalphaolefin is a food grade hydrogenated polyalphaolefin oil, preferably polybutene, polypentene, polyhexene, polyheptene, polyoctene, polynonene, polydecene, polyundodecene, or polydodecene, preferably polydecene.
3. Composition of Claim 1 or 2, **characterized** in that the elastomer is a rubber or a thermoplastic elastomer or thermoplastic vulcanizate or a silicone, preferably a ethylene-propylene-diene rubber, ethylene-propylene rubber, styrene-butadiene rubber, 1,2-syndiotactic polybutadiene rubber, natural rubber, polybutyl rubber, styrene-isoprene-styrene blockcopolymer, styrene-butadiene-(styrene) blockcopolymer, styrene-ethylene-butene-styrene blockcopolymer, or a styrene-ethylene-propylene-(styrene) blockcopolymer.
4. Use of polyalphaolefin as a plastisizer for an elastomer, **characterized** in that a polyalphaolefin or a mixture of polyalphaolefins is added to the elastomer or mixture of elastomers or a mixture containing the elastomer.
5. Use of Claim 4, **characterized** in that the elastomer or the mixture of elastomers is used in an amount ranging between 20 and 95 % by weight, and the polyalphaolefin or the mixture of polyalphaolefins is used in an amount ranging between 5 and 60 % by weight.

6. Use of Claim 4 or 5, characterized in that the polyalphaolefin is a food grade hydrogenated polyalphaolefin oil, preferably polybutene, polypentene, polyhexene, polyheptene, polyoctene, polynonene, polydecene, polyundodecene, or polydodecene, preferably polydecene.

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7. Use according to any of Claims 4 – 6, characterized in that the elastomer is a rubber or a thermoplastic elastomer or thermoplastic vulcanizate or a silicone, preferably a ethylene-propylene-diene rubber, ethylene-propylene rubber, styrene-butadiene rubber, 1,2-syndiotactic polybutadiene rubber, natural rubber, polybutyl rubber, styrene-isoprene-styrene blockcopolymer, styrene-butadiene-(styrene) blockcopolymer, 10 styrene-ethylene-butene-styrene blockcopolymer, or a styrene-ethylene-propylene-(styrene) blockcopolymer.

10

8. Use of the composition according to any of Claims 1 – 3 in medical and medicinal 15 apparatus applications, interior elastomers of automobiles, rubbers of the engine room, seals in passages to the engine room, buffering rubber strips, protective rubbers of joints, isolating materials of cables, cable jackets, seals of food packages, white elastomeric articles and in applications demanding with respect to transparency.

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INTERNATIONAL SEARCH REPORT

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PCT/FI 01/00888

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08L 21/00, C08K 5/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08L, C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI-DATA, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 9844041 A1 (UPOFLOOR OY), 8 October 1998 (08.10.98), abstract, claims --	1-8

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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